IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.	:	09/914,994
Applicants	:	**Mitsuaki Echigo et al.**
Filed	:	September 5, 2001
Title	:	**SYSTEM AND METHOD FOR REMOVING**
	:	**CARBON MONOXIDE**

Group Art Unit	:	1754	Confirmation No.	:	7881
Examiner	:	Ngoc-Yen M. Nguyen	Customer No.	:	28289

DECLARATION UNDER 37 C.F.R §1.132

Commissioner for Patents
P.O. Box 1450
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Sir:

I, _____ Mitsuaki Echigo _____, declare as follows:

1. I have a bachelor degree in synthetic chemistry from Engineering Department of Kyoto University, and a master degree in applied chemistry from Engineering Department of University of Tokyo.

2. The following is my work history.

   1995, April: joined Osaka Gas Co., Ltd.

   1995, October to 1996: research on development of selective reduction catalyst for NOx in exhaust gas

   1995, December to present: research on development of CO-selective removing catalyst for reformed gas

   1996, January to 2002, October: research on polymer electrolyte fuel cell (PEFC)

   2002, November to present: research on development of compact natural gas reformer for PEFC for home use.

3. I am an inventor of the above-identified application and have read and understand U.S. Patent No. 6,290,913 to Aoyama.

{W0136710.1}

4.   Important considerations for developing a fuel cell system incorporating a carbon-monoxide removing system or using a method relating to the subject matter of the above-identified application, include (A) the consumption of hydrogen as the fuel used by the fuel cell system and (B) the balance of energy available by the entire system. These considerations are detailed hereinafter by virtue of an example: treatment of a gas containing 1% or 6,000ppm CO.

A.   Hydrogen Consumption

A-1:   Comparison of hydrogen consumption by CO treatments

There are four options for removing the carbon monoxide: (a) oxidation reaction alone, (b) methanation reaction alone, (c) oxidation reaction followed by methanation reaction and (d) methanation reaction followed by oxidation reaction.

(a) oxidation reaction alone

In this option, an oxidizing agent (e.g. air) is inputted to the treatment-object gas for oxidation of CO. The oxidation reaction of carbon monoxide and the oxidation reaction of hydrogen proceed simultaneously.

Further, as pointed out by the applicant (page 3, lines 1-5) and also by Aoyama (column 17, lines 4-43), 3 moles of oxygen are required, of which 0.5% is consumed for the oxidation of the 1% CO whereas the remaining 2.5% is consumed for the oxidation of hydrogen. That is, 5% of the hydrogen is consumed.

(b) methanation of carbon monoxide alone

In this option, if the methanation reaction takes place selectively, methane and water are produced. Hence, 3% of hydrogen is required and consumed for the 1% CO.

In this case, however, it is not possible to reduce the CO concentration to 10 ppm or lower, which is a targeted reduction of the present invention.

(c) oxidation reaction followed by methanation reaction

In this option, if the first-stage CO remover removes 70% of CO and the second-stage CO remover removes the remaining 30% thereof, the total amounts of hydrogen consumed is: 5 x 0.7 + 3 x 0.3 = 4.4. Hence, 4.4% of hydrogen is consumed in total.

(d) methanation reaction followed by oxidation reaction

Likewise, in this option, if the first-stage CO remover removes 70% of CO and the second-stage CO remover removes the remaining 30% thereof, the total amount of hydrogen consumed is: 3 x 0.7 + 5 x 0.3 = 3.6. Hence, 3.6% of hydrogen is consumed in total.

In summary, for 1% of CO, the consumption hydrogen, including consumption thereof by the remaining oxygen in the respective options, is as follows.

(a) oxidation reaction alone: 5%

(b) methanation alone: 3%

(c) oxidation first (for removal of 70% CO) and then methanation (for removal of remaining 30% CO):   4.4%

(d) methanation first (for removal of 70% CO) and then oxidation (for removal of remaining 30% CO):   3.6%

Hydrogen consumption is the lowest in the case of (b), methanation alone. However, as described hereinbefore, with this method, it is not possible to reduce CO concentration to the targeted level of 10 ppm or lower.

A-2:   Example of hydrogen consumption by CO treatments

The following example is based on the results shown in Table 1, Ex. 2 of the present application.

In this example, the CO concentration at the inlet is 6000 ppm (page 2, lines 4-5) and at shown in the lower row of Table 1, the CO concentration at the outlet of the first CO remover was 1627 ppm and the concentration of the produced methane was 4483 ppm.

Hydrogen consumption is determined according the reaction formulae. The required concentrations are indicated below each substance (all in ppm units).
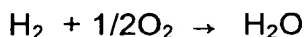
(a) oxidation reaction alone

CO oxidation

$$CO + 1/2O_2 \rightarrow CO_2$$

6000 3000   6000

In the case of CO oxidation, for CO, three moles of oxygen (6000 x 3 = 18000) is required, of which 3000 is used in the oxidation and the remaining 15000 is used in the hydrogen consumption.

H consumption

$$H_2 + 1/2O_2 \rightarrow H_2O$$

30000   15000

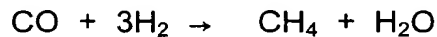Hence, 30000 ppm of hydrogen is consumed in this case.

(b) methanation of carbon monoxide alone

In the case of Ex. 2, the CO concentration at the outlet of the first CO remover is 1627 and the methane concentration is 4483.

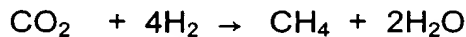Hence, the methanized CO is: 6000 – 1627 = 4373 and the methanized CO_2 is: 4483 – 4373 = 110

This can be expressed in the form of reaction equation as follows.

CO methanization:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

4373   13119   4373

methanization of produced CO_2:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

110   440   110

Hence, 13119 + 440 = 13559 of hydrogen is consumed.

In this case, however, 1627 ppm of CO will remain in the gas.

NOTE: In the following scenarios (c) and (d) the combination of these reactions are based on as assumption that the first stage removes 70% of the CO and the second stage removes 30% of the CO.

(c) oxidation reaction followed by methanation reaction

In the case of Ex. 2, the CO concentration at the outlet of the first CO remover is 1627. Hence, the concentration of CO to be subjected to oxidation is: 6000 – 1627 = 4373. This 4373 of CO is to be oxidized.
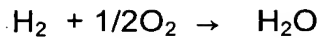
CO oxidation

$$CO + 1/2O_2 \rightarrow CO_2$$

4373 2186.5 4373

In this case, like the case (a) described above, if three moles of oxygen are needed, then, 4373 x 3 – 2186.5 = 10932.5 of oxygen is used in the hydrogen consumption.

H consumption

$$H_2 + 1/2O_2 \rightarrow H_2O$$

21865   10932.5

As the remaining 1627 of CO is to be methanized, like the case (b) described above, when methanization takes place, 1627 x (13559/4373) = 5045 of hydrogen will be consumed.

Consequently, 21865 + 5045 = 26190 ppm of hydrogen in total will be consumed.

(d) methanation reaction followed by oxidation reaction (present invention)
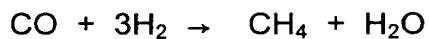
In the case of Ex. 2, the CO concentration at the outlet of the first CO remover is 1627 and the methane concentration is 4483.

Hence, the methanized CO is: 6000 – 1627 = 4373 and the methanized CO_2 is: 4483 – 4373 = 110. Then, the remaining 1627 of CO needs to be removed by the oxidation in the second stage.

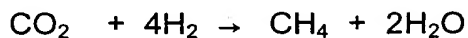These can be expressed in the form of reaction equations as follows.

first stage:

CO methanization:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

4373   13119   4373

methanization of produced CO_2:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

110   440   110

second stage:

CO oxidation:

$$CO + 1/2O_2 \rightarrow CO_2$$
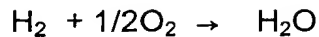
1627   813.5

In this case, like the case (a) described above, if three moles of oxygen are needed, then, 1627 x 3 - 813.5 = 4067.5 of oxygen is used in the hydrogen consumption.

H consumption

$$H_2 + 1/2O_2 \rightarrow H_2O$$

8135   4067.5

Hence, 13119 + 440 + 8135 = 21694 ppm of hydrogen will be consumed.

In summary, for 6000 ppm of CO, the hydrogen consumption including the hydrogen consumption by the remaining oxygen in the respective scenarios is as follows.

(a) oxidation reaction alone: 30000 ppm

(b) methanation alone: 13559 ppm

(c) oxidation first (for removal of 70% CO) and then methanization (for removal of remaining 30% CO):   26910 ppm
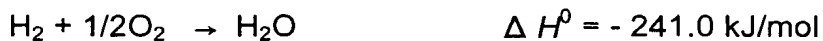
(d) methanization first (for removal of 70% CO) and then oxidation (for removal of remaining 30% CO):   21694 ppm

As discussed, above, excluding the case (b) which is not capable of complete removal of CO, the reaction scheme proposed by the present invention, i.e. (d) methanation reaction followed by oxidation reaction, is more advantageous for reduction of the total amount of hydrogen consumed and required for CO removal.

B. Energy Balance

A methanation reaction and an oxidation reaction both involve the thermal energy generation (in other words, consumption of energy available from the fuel). The amounts are calculated below.

(a)   oxidation reaction

$$CO + 1/2\ O_2 \rightarrow CO_2 \qquad \Delta H^0 = -283.0\ kJ/mol$$
$$H_2 + 1/2O_2 \rightarrow H_2O \qquad \Delta H^0 = -241.0\ kJ/mol$$

(b)   methanation reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H^0 = -205.7\ kJ/mol$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^0 = -164.5\ kJ/mol$$

The above-described two options (c) and (d) involving the combination of these reactions are again based on the same assumption as above of the first stage removing 70% of the CO and the second stage removing 30% of the CO.

(c)   oxidation reaction followed by methanation reaction

CO: 1 mol →   CO: 0.3 mol →   CO: 0 mol

(-283.0 x 0.7) + (-205.7 x 0.3) = - 259.81 kJ

(d)   methanation reaction followed by oxidation reaction

CO: 1 mol →   CO: 0.3 mol →   CO: 0 mol

(-205.7 x 0.7) + (-283.0 x 0.3) = - 228.89 kJ

Disregarding any respective side reactions in the oxidation and methanation reactions, the discharged heat loss is less in process (d) of the present invention (- 228.89 kJ) than in process (c) (- 259.81 kJ). Hence, the thermal energy preserved in an off gas (such as an anode off gas) is greater, thus achieving a higher energy consumption efficiency in a system in which the off gas is recycled.

Further, even when the respective side reactions in the oxidation reaction and the methanation reaction occur with a same selectivity therein, the reaction heat amount (- 164.5 kJ/mol) in the CO_2 methanation reaction as the side reaction of the CO methanation is smaller than that (- 241.0 kJ/mol) in the H_2 oxidation as the side reaction of the CO oxidation. Hence, the discharged heat loss due to the side reaction is also smaller in (d) than in (c).

In the above reaction equations, the consumed amounts of heat energy are denoted with the negative sign. Although the oxidation is an exothermic reaction, if this reaction is viewed from the fuel side, the reaction consumes some of the energy reserved in the fuel. This is the reason for the negative sign notation.

Therefore, oxidation consumes more energy in the treatment of CO than does methanation.

In the case of a fuel cell system including the CO removing system of the present invention, assuming that this system receives a fixed amount of fuel (i.e. total energy input being fixed), it is most advantageous to produce methane in the first stage to preserve this energy as a fuel and then to use it. By reusing the methane produced in the first stage CO remover within the system, efficient utilization of energy can be achieved. By contrast, in a first oxidation reaction producing carbon dioxide, there is no energy preserving compound produced. Therefore, option (d) has significant energy benefits over option (c).

4. In view of the foregoing, a CO treatment process having a methanation step prior to an oxidation step provides superior results (lower hydrogen consumption and higher energy preservation) to a treatment process using the same steps in reverse order. The Aoyama patent does not appreciate the significant benefits achieved using the ordered steps of the method of the present invention.

5. I declare further that all statements made herein of my own knowledge are true and that all statements made on the information and belief are believed to be true, and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable with fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful, false statements may jeopardize the validity of the application or any patent issuing thereon.

___Mitsuaki ECHIGO_____
Name (printed)

___*Mitsuaki Echigo*_____
Signature

___8 / 17 / 2004___
Date

List of Theses

1 : *Enantioselective Synthesis of Dimethyl 3,4-Diphenyladipate by Electroreductive Hydrocoupling of Chiral N-trans- Cinnamoyl-2-oxazolidones*
Naoki Kise, Mitsuaki Echigo and Tatsuya Shono, *Tetrahedron Lett.*, **35**, 1897-1900 (1994).

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3 : *Technology of Fuel Processing (Nenryou Kaishitsu Gijutsu)*
Osamu Okada and Mitsuaki Echigo, in T. Honma (Ed.), Development and Application of PEFC (PEFC no Kaihatsu Gijutsu to Ouyou, Chapter 3.5., BKC Inc., Tokyo, Japan, pp.157-180 (2001).

4 : *Technology of Fuel Processing (Nenryou Kaishitsu Gijutsu)*
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5 : *A Study of CO Removal on an Activated Ru Catalyst for Polymer Electrolyte Fuel Cell Applications*
Mitsuaki Echigo and Takeshi Tabata, *Appl. Catal.* A, **251**, 157-166 (2003).

6 : *Development of Residential PEFC Cogeneration Systems: Ru Catalyst for CO Preferential Oxidation in Reformed Gas*

Mitsuaki Echigo, Norihisa Shinke, Susumu Takami, Seisaku Higashiguchi, Kazuhiro Hirai and Takeshi Tabata, *Catal. Today*, **84**, 209-215 (2003).

7 : *CO Removal from Reformed Gas by Catalytic Methanation for Polymer Electrolyte Fuel Cell Applications*

Mitsuaki Echigo and Takeshi Tabata, *J. Chem. Eng. Japan*, **37**, 75-81 (2004).

8 : *Simulation of the Natural Gas Steam Reforming Process for PEFC Systems*

Mitsuaki Echigo and Takeshi Tabata, *J. Chem. Eng. Japan*, **37**, 723-730 (2004).

9 : *The effects of Coexistent Compounds on CO Preferential Oxidation in Reformed Gas over a Ru Catalyst*

Mitsuaki Echigo and Takeshi Tabata, *J. Chem. Eng. Japan*, **37**, 558-562 (2004).

1 0 : *Performance of a Natural Gas Fuel Processor for Residential PEFC System Using a Novel CO Preferential Oxidation Catalyst*

Mitsuaki Echigo, Norihisa Shinke, Susumu Takami and Takeshi Tabata, *J. Power Sources*, **132**, 29-35 (2004).

1 1 : *Reaction and Surface Characterization studies of Ru/Al_2O_3 Catalysts for CO Preferential Oxidation in Reformed Gas*

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1 2 : *Development of Novel Ru Catalyst of Preferential CO Oxidation for Residential Polymer Electrolyte Fuel Cell System*

Mitsuaki Echigo and Takeshi Tabata, *Catal. Today*, in press.